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High Resolution Study of the r(R)(K=3) Structure of the 3390-A Formaldehyde Band

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16. ABSTRACT

The previously unresolved $^{r}R(K"=3)$ rotational structure of the 3390 Å band ($A^{\sim 1}A_2$-$X^{\sim 1}A_1$) of formaldehyde has been investigated in the range of 29550.5 to 29553.5 cm^{-1} (vacuum) with resolution exceeding 600,000. Magnetic tuning of the silver 3383Å line was utilized to scan this region. The five resolved experimental lines have been assigned to J"=4-8 by interpolation with a least squares fit to the incomplete Dieke and Kistiakowsky data (1934). A questionable shoulder at 29550.99 cm^{-1} may be a $^{r}Q:K"=5,J"=9$ line. The coefficients of a least squares fit of a quadratic in J to the experimental data up to J" = 10 gave values of A'=8.691 ±0.01 cm^{-1} and B'= 1.061 ± 0.01 cm^{-1} in very good agreement with Dieke and Kistiakowsky's data.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Formaldehyde Rotational spectroscopy Zeeman effect High resolution optical spectroscopy Untraviolet absorption spectrum		

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High-Resolution Study of the $^rR(K'' = 3)$ Structure of the 3390-Å Formaldehyde Band

I. INTRODUCTION

The rotational spectra and molecular structure of formaldehyde have been of great interest since the classical analysis of the ultraviolet spectrum by Dieke and Kistiakowsky (*1*) in 1934. Since this early study of the $\tilde{A}^1A_2$–$\tilde{X}^1A_1$ system, numerous investigations have been carried out (*2–6*). However, the 3390-Å ($2_0^1 6_0^1$) band has received little attention in these studies. Dieke and Kistiakowsky were able to assign observed lines in the 3390-Å band to ^pP, ^pQ, ^rQ, and ^rR branches for $K'' = 3$. However, they were unable to resolve the lines in the center of the bands.

An instrument has been developed (*7*) to magnetically scan molecular absorption spectra with a resolution exceeding 600 000. An atomic emission line from a lamp is split by imposition of a magnetic field, and the polarized Zeeman components are used to scan the molecular feature of interest. The scanning range of both components is limited to approximately 3 cm^{-1}, but the resolution is very high due to the narrow width of the atomic probe line. Because of the inherent high resolution of this instrument, the previously unresolved region of the $K'' = 3$, ^rR branch of formaldehyde was studied to determine its nature. The resulting resolved lines were assigned and estimated values of A' and $\bar{B}'$ for the $K'' = 3$, ^rR branch were obtained.

II. EXPERIMENTAL DETAILS

Formaldehyde vapor was produced from paraformaldehyde and introduced into a 25-cm path length absorption cell at 25°C. The formaldehyde was present at a few Torr pressure. The lamp, which was mounted between the poles of a 4-in. Varian electromagnet, had a cathode of silver. The cathode had dc (110 V, 50 mA) and RF (70 MHz, 10 W) simultaneously applied (*8, 9*), as argon flowed at 5 Torr through the lamp. The magnetic field (0 to 25 kgauss) was applied to the discharge plasma in the direction parallel to the direction of observation. After passing through the sample, the circularly polarized Zeeman components were converted into linearly polarized light with a photoelastic retarder and separated with a Rochon prism.

A JY HR20 monochromator was used to isolate the silver 3383-Å line from the source. Initially, separate scans were made to higher (σ^+ component) or lower energy (σ^- component) relative to the zero field energy of 29 552.01 cm^{-1} (vacuum) with a maximum of 25 kgauss field strength. This corresponds to a scan of ±1.5 cm^{-1} relative to the 29 552.01-cm^{-1} unsplit silver line position. No absorption bands were found in the region of 29 552 to 29 553.5 cm^{-1} (σ^+ scan). Therefore, to obtain a better signal/noise ratio, the linear polarizer was rotated on the optical

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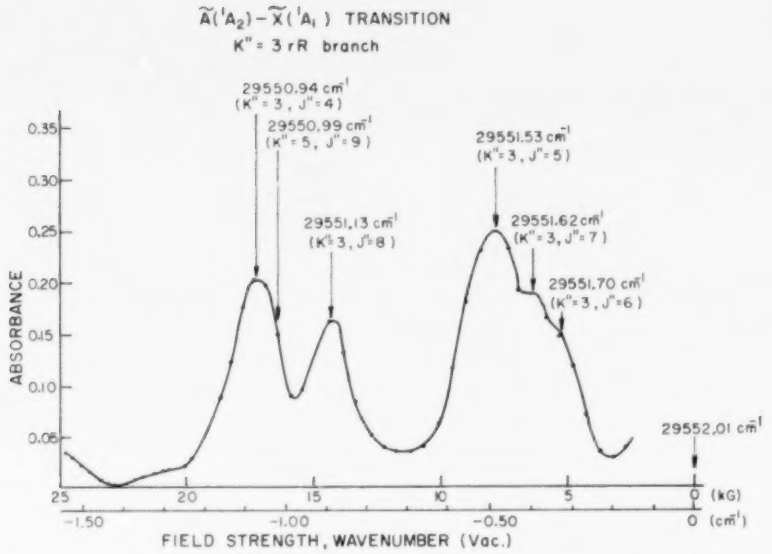

FIG. 1. Zeeman scanning of formaldehyde spectrum with Ag 3383-Å line.

axis at 3600 rpm; and the difference between the σ^- and σ^+ spectrum was recorded. Further details concerning the apparatus are given elsewhere (*7*).

III. RESULTS AND CONCLUSIONS

The high-resolution scan of the spectral region from 29 552.0 to 29 550.5 cm^{-1} (vacuum) is shown in Fig. 1. No absorption features were found in the 29 552- to 29 553.5-cm^{-1} region. There are three distinct lines at 29 550.94, 29 551.13, and 29 551.53 cm^{-1}. Two other obvious lines at 29 551.62 and 29 551.70 cm^{-1} partially overlap the more intense 29 551.53-cm^{-1} line. A less obvious, even questionable, shoulder occurs at 29 550.99 cm^{-1}. These features occur in the region of the $K'' = 3$, $'R$ branch which was not resolvable in the original work of Dieke and Kistiakowsky. Table I summarizes the experimental data from Dieke and Kistiakowsky for the $'R$, $K'' = 3$ low-J lines and the locations of the lines from the present work. The estimated accuracy of our data set is ± 0.03 cm^{-1}.

The $J'' = 5, 6, 7$ lines were unresolved in the 1934 study. The $J'' = 4$ line was also unresolved from a $'Q$, $K'' = 5$, $J'' = 9$ line at 29 550.99 cm^{-1}. In order to assign the experimentally observed five lines from the present study to the $'R$ branch, a least-squares fit of a polynomial in J^4 was made to the Dieke and Kistiakowsky data for $J'' = 3, 4, 8$–13, 15, and 17. The interpolated energies for the unresolved $J'' = 5, 6, 7$ lines are given in Table I. The predicted energies from this procedure for resolved lines up to $J'' = 10$ agree with the 1934 data to within ± 0.01 to 0.02 cm^{-1}. The expected accuracy for the unresolved lines is thus ± 0.02 cm^{-1}. Comparisons of our experimental data with the predicted values gives immediately the

TABLE I

Assignments of $'R$ Rotational Bands of Formaldehyde near 3383 Å

Assignment	Dieke and Kistiakowsky	Interpolated[b]	This Study[c]
^rR: K"=3	(cm^{-1})	(cm^{-1})	(cm^{-1})
J"=3	29550.13	29550.12	
4	29550.99[a]	29551.00	29550.94
5	29551.57[d]	29551.53	29551.53
6	29551.57[d]	29551.72	29551.70(s)[e]
7	29551.57[d]	29551.58	29551.62(s)[e]
8	29551.11	29551.12	29551.13
9	29550.35	29550.34	
10	29549.26	29549.24	
^rQ:K"=5,J"=9	29550.99		29550.99(?)[f]

a. An unresolved ^rQ band also occurs at this energy.

b. Predicted from a least squares fit of a polynominal in J^4 to experimental data for J" = 3, 4, 8, 9, 10, 11, 12, 13, 15, 17.

c. Accurate to within ±0.03 cm^{-1}.

d. Unresolved.

e. Shoulder.

f. Questionable shoulder at this energy.

assignments $J'' = 5$ (29 551.53); $J'' = 6$ (29 551.70), $J'' = 7$ (29 551.62). All agree within ±0.06 cm^{-1} of the interpolated values including the two shoulders. Our results for the $J'' = 4$ and $J'' = 8$ lines agree with the Dieke and Kistiakowsky data to within ±0.05 cm^{-1}, i.e., within the combined experimental errors. The questionable shoulder in our results at 29 550.99 cm^{-1} can be assigned as the $'Q$, $K'' = 5$, $J'' = 9$ line given at the same energy by Dieke and Kistiakowsky.

To verify the assignments given above, the combined set of data (Dieke and Kistiakowsky and ours) for the $'R$ branch, $K'' = 3$, $J'' = 3$–10 energies was fitted by least squares to a polynomial in J^2. The experimental data were reproduced to within an RMS error of ±0.013 cm^{-1} by this equation. The coefficients of J^2, J, and the constant in the equation were −0.163344, 1.99725, and 29 545.6142 cm^{-1}, respectively. For a prolate near symmetric top with neglect of centrifugal distortion terms, the $K'' = 3$, $'R$ transition energies are

$$\nu = [\nu_0 + 16A' - 14\bar{B}' - 9(A'' - \bar{B}'')] + J[3\bar{B}' - \bar{B}''] + J^2[\bar{B}' - \bar{B}''].$$

It follows immediately that $\bar{B}' - \bar{B}'' = -0.163344$ cm^{-1}, $3\bar{B}' - \bar{B}'' = 1.99725$ cm^{-1}, and $\nu_0 + 16A' - 14\bar{B}' - 9(A'' - \bar{B}'') = 29\,545.6142$ cm^{-1}. Using the ground-state data (*4*) of $A'' = 9.405524$ cm^{-1}, $\bar{B}'' = 1.214811$ cm^{-1}, and $\nu_0 = 29\,495.12$ cm^{-1} (*1*) in these relationships yields

$$\bar{B}' = 1.061 \pm 0.01 \text{ cm}^{-1},$$

$$A' = 8.691 \pm 0.01 \text{ cm}^{-1}.$$

These agree very well with $\bar{B}' = 1.056$ cm^{-1}, $A' = 8.701$ cm^{-1} reported by Dieke and Kistiakowsky for $K' = 4$.

The use of symmetric-top equations above may be questioned. Formaldehyde is very nearly a prolate symmetric top in its ground state with $b'' = -0.00984$ (*4*). In the excited state $b' = -0.0084$ (*1*). Calculations of the asymmetry splitting and corrections to the symmetric-top equations for the J and K ($K \geq 3$, $J \leq 10$) values considered were performed using an expansion in powers of b to determine their magnitude. For the worst case, the asymmetry splitting was less than 0.002 cm^{-1}, and the deviation from the symmetric-top transition energy was less than 0.05 cm^{-1}. The neglect of centrifugal distortion terms was necessitated by the large number of excited-state constants required. Estimates of the magnitude of these terms gave results of less than 0.1 cm^{-1}.

Based upon the rotational constants obtained, the assignments of the previously unresolved lines of the $'R$, $K'' = 3$ branch are reasonable. It is interesting to note that the present results were obtained on a desk-size apparatus whereas the lines were not resolved with a 40-ft spectrograph. The statement made by Dieke and Kistiakowsky (*1*) that the inherent rotational linewidths precluded their resolution also seems to be proved incorrect by this study. The line width of the $K'' = 3$, $J'' = 8$ line (FWHM) is approximately 0.13 cm^{-1}.

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